Relativistic general-order coupled-cluster method for high-precision calculations: Application to Al$^+$ atomic clock

Mihály Kállay[1], B. K. Sahoo[2], H. S. Nataraj[1], B. P. Das[3], and Lucas Visscher[4]

[1] *Department of Physical Chemistry and Materials Science,*
Budapest University of Technology and Economics, Budapest P.O.Box 91, H-1521 Hungary
[2] *Theoretical Physics Division, Physical Research Laboratory, Ahmedabad 380009, India*
[3] *Indian Institute of Astrophysics, 560034 Bangalore, India and*
[4] *Amsterdam Center for Multiscale Modeling, VU University Amsterdam,*
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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We report the implementation of a general-order relativistic coupled-cluster method for performing high-precision calculations of atomic and molecular properties. As a first application, the static dipole polarizabilities of the ground and first excited states of Al$^+$ have been determined to precisely estimate the uncertainty associated with the BBR shift of its clock frequency measurement. The obtained relative BBR shift is -3.66 ± 0.44 for the $3s^2 \, {}^1S_0^0 \to 3s3p \, {}^3P_0^0$ transition in Al$^+$ in contrast to the value obtained in the latest clock frequency measurement, -9 ± 3 [Phys. Rev. Lett. **104**, 070802 (2010)]. The method developed in the present work can be employed to study a variety of subtle effects such as fundamental symmetry violations in atoms.

The role of high precision calculations of various properties of heavy atoms and molecules which support the state-of-the-art measurements has gained incredible importance in recent years. This is particularly true in the context of atomic clocks [1], probes of fundamental symmetry violations [2–4], and search for the variation in the fundamental constants [5]. The relativistic coupled-cluster (CC) method with single and double excitations (CCSD) supplemented by the important triple excitations has yielded reasonably accurate results [2–4]. However, an extension to this method by including higher order excitations and its application to large systems are extremely challenging. The general nonrelativistic CC approach of Kállay and co-workers provides one of the most efficient routes to the incorporation of higher order excitations by exploiting the features of the many-body diagrammatic techniques and string algebra [6].

In this Letter, we extend the general-order nonrelativistic CC work reported in Ref. [6] to the relativistic framework aiming to apply it for high-precision studies in several important areas of fundamental physics; to mention a few: atomic clocks, parity non-conservation (PNC), electric dipole moment (EDM) due to parity and time reversal violations. As a proof-of-principle, we have employed the method for the calculation of the blackbody radiation (BBR) shift in the $3s^2 \, {}^1S_0^0 \to 3s3p \, {}^3P_0^0$ clock transition of Al$^+$. This transition provides the basis for the most accurate atomic clock to date [1, 5, 7], for which the fractional frequency inaccuracy has recently been estimated as 8.6×10^{-18} [5]. Although the size of the BBR shift in the Al$^+$ clock is smaller than those in most of the other ions considered for atomic clocks, the associated uncertainty in the estimated BBR shift is about 35% of the total uncertainty. The BBR shift was also obtained using the static polarizabilities calculated from the oscillator strengths taken from different sources [8], and it was investigated later by Mitroy *et al.* [9] along similar lines using the configuration interaction (CI) method with a semi-empirical core potential. Other nonrelativistic calculations also provide results that agree with each other [10–12].

With the general-order relativistic CC method, we also consider the linear response theory which is the first application of its kind to atoms for the calculation of static polarizabilities of the ground and first excited states of Al$^+$. This method allows for the precise calculations of the ground-state and one-hole and one-particle excited-state properties, and it can be suitably modified for applying it to PNC and EDM studies in the proposed atoms such as Ra and Yb [13, 14].

The exact wave function in the CC theory involves an exponential parameterization of the form:

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}}|0\rangle \tag{1}$$

where $|0\rangle$ is the Dirac-Fock (DF) reference determinant, and the cluster operator $\hat{T}$ can be decomposed as

$$\hat{T} = \sum_{k=1}^{n} \hat{T}_k \tag{2}$$

where $\quad \hat{T}_k = \sum_{\substack{a_1 < a_2 \ldots < a_k \\ i_1 < i_2 \ldots < i_k}} t_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k} \, a_1^+ i_1^- a_2^+ i_2^- \ldots a_k^+ i_k^- \tag{3}$

The convention followed here is that indices i (a) refer to occupied (virtual) spinors in the reference determinant. Projecting onto the excited determinants defined by $|\Psi_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k}\rangle = a_1^+ i_1^- a_2^+ i_2^- \ldots a_k^+ i_k^- |0\rangle$ we get the nonlinear algebraic equations for the correlation energy E and

unknown cluster amplitudes for the excitation of any order as

$$\langle \Psi_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k} | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | 0 \rangle \;=\; E \delta_{k,0}, \quad (k = 1, \ldots n), \quad (4)$$

where $\hat{H}_N$ is the normal-ordered Dirac-Coulomb (DC) Hamiltonian and k is the level of excitation. The CC approaches corresponding to the $n = 2, 3, 4, \ldots$ values, i.e., the CC singles and doubles (CCSD), CC singles, doubles, and triples (CCSDT), CC singles, doubles, triples, and quadruples (CCSDTQ), ...methods constitute a hierarchy, which converges to the exact solution of the Dirac equation in the given one-particle basis set.

The excitation energies are obtained invoking the linear-response CC (LR-CC) theory as given in Refs. [15] and [16]. In LR-CC theory the excitation energies ω are calculated by determining the right-hand eigenvalues of the CC Jacobian as

$$\langle \Psi_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k} | \left[e^{-\hat{T}} \hat{H}_N e^{\hat{T}}, \hat{R} \right] | 0 \rangle \;=\; \omega \, r_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k}, \qquad (5)$$

where operator $\hat{R}$ has the same structure as the cluster operator with parameters $r_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k}$.

As it is well-known, the energy of the ith state of an atom placed in an isotropic electric field of strength ε changes as

$$E_i(\varepsilon) = E_i(0) - \frac{\alpha_i}{2} \varepsilon^2 - \ldots, \qquad (6)$$

where $E_i(0)$ and $E_i(\varepsilon)$ are the total energies of the state i in the absence and the presence of the field, respectively, and α_i is the static dipole polarizability of state i. The BBR shift for a transition $|J_i, M_i\rangle \to |J_j, M_j\rangle$ is the shift of the corresponding transition energy due to the finite background thermal radiation. At temperature T, neglecting the dynamic correction factor from the previous finding [9], in the adiabatic expansion it is given by

$$\Delta E_{ij}^{\text{BBR}} = -\frac{1}{2}(831.9 \text{ V/m})^2 \left(\frac{T(\text{K})}{300} \right)^4 (\alpha_i - \alpha_j). \quad (7)$$

Consequently the evaluation of the BBR shift requires the knowledge of the static polarizabilities for the two states involved in the clock transition.

It is obvious from Eq. (6) that the static polarizability can be evaluated as the second derivative of $E_i(\varepsilon)$ with respect to ε. In our study we followed this approach and calculated the polarizabilities by numerical differentiation. The total energies were computed with and without the perturbation; here the perturbation was taken to be $-D \cdot \varepsilon$ where D is the induced electric dipole moment, and the values of the electric field ε were fixed to 1×10^{-3} and 2×10^{-3} a.u. The polarizabilities were obtained from the resulting three energy values assuming that they lie on a quartic polynomial. With the test calculations the numerical error of this procedure was found to be negligible.

TABLE I: Calculated excitation energies (cm^{-1}) and polarizabilities (a.u.)

	Excitation energy	Polarizability		
		Ground state	Excited state	Differential
t-aug-cc-pCVDZ (1s, 2s, and virtuals > 5E$_h$ are frozen)				
CCSD	37222	24.215	24.380	0.165
CCSDT	37324	24.158	24.357	0.199
CCSDTQ	37326	24.156	24.358	0.202
t-aug-cc-pCVDZ				
CCSD	37005	24.203	24.261	0.058
CCSDT	37167	24.072	24.208	0.136
t-aug-cc-pCVTZ				
CCSD	37228	24.143	25.040	0.897
CCSDT	37373	24.017	24.979	0.962
t-aug-cc-pCVQZ				
CCSD	37160	24.273	24.700	0.427
t-aug-cc-pCV5Z				
CCSD	37186	24.251	24.656	0.406

In oder to approach the exact solution of the Dirac-Coulomb equation for the Al$^+$ ion as closely as possible, the convergent hierarchy of CC methods was combined with the convergent basis sets in the total energy calculations. The ground-state energies were obtained using the CCSD, CCSDT, and CCSDTQ methods, while excited-state energies were determined by the LR-CC method in the same excitation manifold. The one electron basis sets used were Dunning's triply-augmented correlation consistent polarized core-valence X-tuple-ζ sets [17, 18] abbreviated as t-aug-cc-pCVXZ, where X is the so-called cardinal number of the basis set, $X = $ D, T, Q, and 5 for double-, triple-, quadruple-, and pentuple-ζ basis sets, respectively. The basis sets were uncontracted in all the calculations. The CC calculations were carried out with our new all-order relativistic CC code implemented in the MRCC suite [19]. The transformed molecular orbital integrals were generated by the DIRAC package [20].

To give an accurate estimate of the properties we studied, we adopted a composite scheme, which is well-established in quantum chemistry and widely used for highly-accurate calculations of molecular properties (see, e.g., Refs. [21–25]), in which the calculations with a particular method in the CC hierarchy are carried out with the largest possible basis set and the largest possible number of correlated electrons. In practice, CCSD and CCSDT calculations were performed with pentuple- and triple-ζ basis sets, respectively, correlating all electrons and all orbitals. CCSDTQ calculations were only feasible with the t-aug-cc-pCVDZ basis set, but further approximations were necessary even in this basis, and the 1s and 2s electrons were frozen as well as the virtual orbitals lying above 5 E$_h$ were dropped. Our final esti-

TABLE II: Composite excitation energies (cm^{-1}), polarizabilities (a.u.), and their estimated errors. Note that 1s, 2s, and the virtual orbitals above 5 E$_h$ were frozen for the CCSDTQ-CCSDT calculations.

Contribution	Excitation energy	Polarizability			Source
		Ground state	Excited state	Differential	
CCSD	37186±25	24.251±0.022	24.656±0.044	0.406±0.021	t-aug-cc-pCV5Z
CCSDT-CCSD	146±33	−0.126±0.011	−0.061±0.015	0.065±0.026	t-aug-cc-pCVTZ
CCSDTQ-CCSDT	2±4	−0.002±0.005	0.001±0.002	0.003±0.007	t-aug-cc-pCVDZ
Breit+QED	−6±6	0.015±0.015	0.018±0.018	0.003±0.003	Numerical MCDF
Composite	37326±68	24.137±0.053	24.614±0.078	0.477±0.057	Sum of all contributions

mates were obtained by adjusting the pentuple-ζ CCSD values with the CCSDT-CCSD and CCSDTQ-CCSDT increments computed with the triple- and double-ζ basis sets, respectively. The error of our computed values were estimated on the basis of the convergence pattern of the results. To improve the results further, we estimated the contributions from Breit interaction and QED corrections using the numerical multi-configurational DF (MCDF) method as implemented in the MCDFGME program [26] and the sum-over-states expression for polarizabilities [9].

The calculated polarizabilities are compiled in Table I where we also present the excitation energy of the clock transition. Since the latter is precisely known from experiments, the performance of our approach can be partly judged from the agreement of our calculated and the measured excitation energy.

The convergence of both the polarizabilities and excitation energies with increasing levels of correlation is rapid. The CCSD values themselves are reliable; further, the contribution of triple excitations to both properties is less than 1%. Interestingly the polarizability of the ground-state is more sensitive to correlation effects than the excited-state: the effect of triple excitations for the ground state is twice as large as that for the excited state, viz. 0.13 a.u. vs. 0.06 a.u. The magnitude of the triples contribution to the polarizability shift is also moderate, it only amounts to 0.06 a.u., however, it is more than 10% of the composite value and thus cannot be ignored. The effect of quadruple excitations is approximately two orders of magnitude smaller than that of the triples and can be considered as negligible, which also implies that higher-order correlation contributions can safely be ignored.

The basis set convergence of the properties we have studied is in accordance with the usual trend—relatively slow, but the results are close to the basis set limit when large basis sets are employed. The polarizabilities and excitation energies are already reliable in the smaller basis sets, while the polarizability shift, which is a small difference of two large numbers, requires at least quadruple-ζ-quality basis set even for a qualitatively correct result. It is interesting to note that in this case the polarizability of the excited-state is more sensitive to the quality of the basis set than the ground state. From the compari-

son of the quadruple- and pentuple-ζ results we observe that the CCSD excitation energies and polarizabilities change on the scales of 10 cm^{-1} and 0.01 a.u., respectively, which means that the relative change is about 0.1% for both properties. Since the basis-set error decreases monotonically with the size of the basis set, the error with respect to the infinite basis set limit is also expected to be less than 0.1%. Unfortunately the errors of the ground- and excited-state polarizabilities do not cancel each other, and consequently the absolute error of the CCSD polarizability shift is larger. For the aforementioned reason its relative error is also significantly larger, a couple of percent of the total value. Similar conclusions can be drawn for the contribution of triple excitations. The CCSDT-CCSD difference also changes in the 10 cm^{-1} and 0.01 a.u. range for excitation energies and polarizabilities, respectively, when going from the double- to the triple-ζ basis set, and the change in the polarizability shift is only 0.013 a.u. Thus the error in our final estimates stemming from the calculations of the triples contribution is also smaller than 0.1% (3%) for the excitation energy and polarizabilities (polarizability shift).

TABLE III: Comparison of theoretical and experimental polarizabilities (a.u.), and relative BBR shifts.

Polarizability		BBR shift	Reference
$3s^2\,^1S_0^0$	$3s3p\,^3P_0^0$	×10^{18}	
24.19			[10]
24.83±5.26	24.63±4.93	−8±3	[8]
24.20±0.75			[11]
24.12			[29]
24.14±0.12	24.62±0.25	−4.18±3.18	[9]
24.22±1.21	24.78±1.24	−4.3±2.5	[30]
24.14±0.05	24.61±0.08	−3.66±0.44	This work

The calculation of the properties that have been investigated using the composite approach outlined above is shown in Table II in detail, where we also present our error estimates based on the convergence of the contributions with the basis set. It has been found in numerous studies that in the higher members of correlation-consistent basis set family the basis set error for various properties is usually reduced by a factor of at least two when increasing the cardinal number of the basis set

by one. The reduction of the basis set error would also be valid for the current properties. In fact, the ratio of the quadruple-ζ−triple-ζ and pentuple-ζ−quadruple-ζ differences of CCSD excitation energies, ground- and excited-state polarizabilities, and polarizability shifts is 2.7, 5.8, 7.8, and 22.1, respectively. Thus we presume that the entire difference between the pentuple- and quadruple-ζ results is a conservative estimate for the basis set error of the CCSD values, and we attach these numbers as error bars. The estimation of the intrinsic error of the CCSDT-CCSD contributions is less straightforward since the results are not available in the larger basis sets. Therefore we take twice the difference between the double- and the triple-ζ triples contributions as a conservative choice. The quadruples contribution, i.e., the CCSDTQ-CCSDT difference is only available in one basis set, and no conclusion about its basis set dependence can be drawn. Consequently we take twice the entire contribution as the error bar. The contribution of Breit and QED corrections for the excitation energy is ~ -6 cm^{-1} while for polarizabilities of the ground and excited states it is 0.015 and 0.018 a.u., respectively. We would like to remark that these effects are computed using numerical orbitals at the DF level of the theory and hence they are devoid of any basis set incompleteness errors. As the missing correlation contribution to these effects is not expected to exceed its DF value, we have taken the entire value itself as the upper limit of the error.

For the excitation energy a highly-accurate experimental value, 37393±0 cm^{-1} is available [1], thus the agreement between the experimental and our best calculated excitation energy, 37326±68 cm^{-1} is very good and the deviation is within 0.2% of the experimental energy.

We compare our polarizabilities and the BBR shift to the previous theoretical and empirical results in Table III. Our results are in good agreement with the previous computational results, however, more accurate than the latter. In contrast, there is a considerable discrepancy between the present and the experimental BBR shift. There is a brief discussion on various approaches employed to calculate the polarizabilities and the BBR shift by Mitroy *et al.* [9], hence we do not repeat them here, however we would like to emphasize that our results are the first *ab initio* values based on a relativistic framework.

In conclusion, we have developed a general-order relativistic coupled-cluster method for high-precision calculations in atoms and molecules. Using this method the ground-state, excited-state, and differential polarizabilities of the Al$^+$ ion are obtained to be 24.14±0.05, 24.61±0.08, and 0.48±0.06 a.u., respectively. From the latter value and the measured clock frequency of $1.121015393207851 \times 10^{-15}$ Hz [5] we obtain −0.0041±0.0005 Hz for the absolute and −3.66±0.44 for the relative BBR shift. It is the most accurate estimate of the BBR shift in Al$^+$, using which the systematic shift in the above frequency measurement can be obtained as $(-1112.46 \pm 6.04) \times 10^{-18}$ against the value of $(-1117.8 \pm 8.6) \times 10^{-18}$ considered in Ref. [5].

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